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PATENT OFFICE

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(19) (CA) CANADIAN PATENT (12)

(54) Carbonate-Supported Catalytic System for Epoxidation of  
Alkenes

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(73) Union Carbide Corporation , U.S.A.

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10                    IMPROVED CARBONATE-SUPPORTED  
                  CATALYTIC SYSTEM FOR  
                  EPOXIDATION OF ALKENES

Technical Field:

15                  The present invention is directed to an improved system for the preparation of alkene oxide from alkene and an oxygen-containing gas employing a supported silver catalyst and to the catalysts used in the system. More particularly, the present invention relates to the oxidation of alkenes to the corresponding epoxides in which enhanced performance is attained by combination of a gaseous member of a redox-half reaction pair present in the gaseous mixture of oxygen and alkene, a salt of a member of a redox-half reaction pair in combination with the catalyst and use of a stability-enhancing carbonate salt support.

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Background Art:

30                  The production of alkene oxides, or epoxides, particularly ethylene oxide by the direct oxidation of the corresponding alkene in the presence of a silver-containing catalyst has been known for many years. For example, the basic process was described by Lefort in U. S. Patent 1,998,878 and by Van Peski

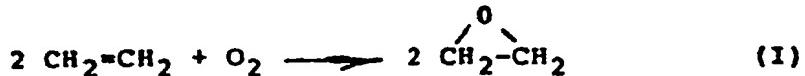
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in U. S. Patent 2,040,782. The basic reaction proceeds, as illustrated for ethylene, according to the equation:

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and production of an unwanted by-product according to the reaction:

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or by further oxidation of the epoxide.

In the years between the Van Peski patent and  
15 the present inventions, research efforts have been directed to improving both the activity and longevity or useful life of the catalyst and the efficiency of the overall catalytic reaction. As is indicated by reactions I and II, the oxidation of an alkene may  
20 produce either the alkene oxide (I) sought in the process or the by-products CO<sub>2</sub> and H<sub>2</sub>O.

Several terms are commonly used to describe some of the parameters of the catalytic system. For instance, "conversion" has been defined as the percentage of alkene fed to the reactor which undergoes reaction. The "efficiency" or, as it is sometimes called, the "selectivity" of the overall process is an indication of the proportion, usually represented by a percentage, of the converted material or product  
25 which is alkene oxide. The commercial success of a reaction system depends in large measure on the efficiency of the system. At present, maximum efficiencies in commercial production of ethylene oxide by epoxidation are in the low 80s, e.g., 80 or 81 percent.  
30 Even a very small increase in efficiency will  
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provide substantial cost benefits in large-scale operation. For example, taking 100,000 metric tons as a typical yearly yield for a conventional ethylene oxide plant and assuming 80 percent conversion, an 5 increase in efficiency of from 80 to 84 percent, all other things being equal, would result in a savings of 3790 metric tons of ethylene per year. In addition, the heat of reaction for reaction II (formation of carbon dioxide) is much greater than that of reaction I (formation of ethylene oxide) so heat-removal problems are more burdensome as the efficiency decreases. Furthermore, as the efficiency decreases, there is the potential for a greater amount of impurities to be present in the reactor effluent which can 10 complicate separation of the desired alkene oxide product. It would be desirable, therefore, to develop a process for the epoxidation of alkene in which the efficiency is greater than that obtained in conventional commercial processes, e.g., with ethylene, efficiencies of 84 percent or greater, while maintaining other performance characteristics, particularly the activity, as described below, in a satisfactory range.

The product of the efficiency and the conversion 25 is equal to the yield, or the percentage of the alkene fed that is converted into the corresponding oxide.

The "activity" of the catalyst is a term used to indicate the amount of alkene oxide contained in the 30 outlet stream of the reactor relative to that in the inlet stream. Activity is generally expressed in terms of pounds of alkene oxide produced per cubic foot of catalyst per hour at specified reaction conditions and rate of feed. The activity may also be 35 stated in terms of the amount of ethylene oxide in

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the outlet stream or the difference between the ethylene oxide content of the inlet and outlet streams.

If the activity of a reaction system is low, then, all other things being equal, the commercial value of that system will be low. The lower the activity of a reaction system, the less product produced in a unit time for a given feed rate, reactor temperature, catalyst, surface area, etcetera. A low activity can render even a high efficiency process commercially impractical. For production of ethylene oxide, an activity below 4 pounds of ethylene oxide per hour per cubic foot of catalyst is unacceptable for commercial practice. The activity is preferably greater than 8 pounds, and in some instances an activity greater than 11 pounds of alkene oxide per hour per cubic foot of catalyst is desired.

In some instances, activity is measured over a period of time in terms of the amount of alkene oxide produced at a specified constant temperature. Alternatively, activity may be measured as a function of the temperature required to sustain production of a specified constant amount of alkene oxide. Plots of such measurements yield "aging rates" which reflect the stability or useful life of the catalyst. The useful life of a reaction system is the length of time that reactants can be passed through the reaction system during which acceptable activity is observed. The area under a plot of activity versus time is equal to the number of pounds of alkene oxide produced during the useful life of the catalyst per cubic foot of catalyst. The greater the area under such a plot, the more valuable the process is since regeneration or replacement of the catalyst involves a number of expenses, sometimes referred to as turnaround costs. The rate at which activity decreases,

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i.e., the rate of deactivation at a given point in time, can be represented by the slope of the activity plot, i.e., the derivative of activity with respect to time:

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$$\text{deactivation} = d[\text{activity}] / dt.$$

The average rate of deactivation over a period of  $t$  we can be represented then by the change in 10 activity divided by the time period:

$$\text{average deactivation} = \Delta \text{activity} / \Delta t.$$

At some point, the activity decreases to an 15 unacceptable level, for example, the temperature required to maintain the activity of the system becomes unacceptably high or the rate of production becomes unacceptably low. At this point, the catalyst must either be regenerated or replaced. Some of 20 these definitions may be represented as set out below:

Conversion =  $\frac{\text{moles alkene reacted}}{\text{moles alkene fed}} \times 100$

25

Efficiency =  $\frac{\text{moles alkene oxide produced}}{\text{moles alkene reacted}} \times 100$

30

Yield =  $\frac{\text{moles alkene oxide produced}}{\text{moles alkene fed}} \times 100$

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Typically, in commercial production, since the outlet or effluent stream emanating from the reactor may contain substantial amounts of unreacted alkene, the effluent stream is recycled and combined with the

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feedstream after removal of at least a portion of the alkene oxide. Generally, as the activity of a catalyst decreases with time, in order to obtain the same ultimate yield of epoxide product, the effluent stream must either be recycled a greater number of times or the temperature within the reactor must be raised to increase the activity of the catalyst. The former approach to increasing the yield of product requires additional energy expenditures and the latter, which is most frequently used, causes faster catalyst deterioration.

As used herein, an activity-reducing compound refers to a compound which, when present in an activity-reducing amount, causes a reduction in activity, some or all of which activity may subsequently be regained by returning to a situation in which the concentration of the compound is below the minimum activity-reducing amount. The minimum activity-reducing amount varies depending on the particular system, the feedstream and the activity-reducing compound.

Conversely, deactivation, as used herein, refers to a permanent loss of activity, i.e., a decrease in activity which cannot be recovered. As noted above, activity can be increased by raising the temperature, but the need to operate at a higher temperature to maintain a particular activity is representative of deactivation. Furthermore, catalysts tend to deactivate more rapidly when reaction is carried out at higher temperatures.

In contrast to problems associated with low or decreasing catalyst activities, less than satisfactory efficiencies result in loss of starting material, the alkene, as the unwanted product CO<sub>2</sub>. Ultimately, this also increases product costs.

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To be considered satisfactory, a catalyst must not only have a sufficient activity and the catalytic system provide an acceptable efficiency, but the catalyst must also demonstrate a minimum useful life or stability. When a catalyst is spent, typically the reactor must be shut down and partially dismantled to remove the spent catalyst. This results in losses in time and productivity. In addition, the catalyst must be replaced and the silver salvaged or, where possible, regenerated. Even when a catalyst is capable of regeneration in situ, generally production must be halted for some period of time. At best, replacement or regeneration of catalyst requires additional losses in time to treat the spent catalyst and, at worst, requires replacement of the catalyst with the associated costs.

Since even small improvements in activity, efficiency or useful life may have significance in large scale commercial production, such improvements have been the object of a great deal of research in the direct epoxidation of alkenes. The focus of attempts to improve performance, such as the activity and useful life of the catalyst and the efficiency of the system, has included such areas as feedstream additives or removal of components therefrom; methods of preparation of the catalyst; deposition or impregnation of a particular type or form of silver; composition, formation, physical properties and morphology of the support; additives deposited on or impregnated in the support; shape of support aggregates used in the reactor; and various types of reactors and bed designs, such as stationary and fluidized beds.

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Early work on the silver-catalyzed direct oxidation of alkenes to alkene oxides in many instances resulted in improvements in activity and particularly the selectivity of the system, in many cases the efficiency increasing by several percent. Recent modifications in such systems have resulted in only small incremental improvements in efficiency; however, in terms of operating costs, even fractions of a percent improvement in efficiency can translate into large savings in production. Accordingly, current research is still being directed to improvements in the activity and useful life of the catalyst and selectivity of the system.

Although a vast number of elements and compounds are known to have effective catalytic properties in various reactions, many have at least one shortcoming, such as very high cost and/or limited availability, thermal instability in the temperature range in which the reaction is to be conducted, low mechanical strength, small surface area per unit of volume, susceptibility to poisoning, short useful lifetime, etcetera. Such undesirable characteristics make such substances of limited utility as catalysts. Some of these shortcomings, however, may be overcome and in some instances the effectiveness of the catalyst may be improved by applying the substance to a carrier or support.

New support materials are continuously being tried. However, many of those which were employed in the early development of the silver-bearing catalysts are, with some modifications, still being used. Materials which have found most widespread use are typically inorganic and generally are of a mineral nature. Such materials commonly include alumina, fire brick, clay, bauxite, bentonite, kieselguhr,

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carbon, silicates, silica, silicon carbide, zirconia, diatomaceous earth, and pumice.

In addition to the physical strength of the support materials, other physical properties, such as 5 surface area, pore volume, pore dimensions, and catalyst size have drawn considerable attention. These properties have been examined with great scrutiny when evidence indicated that there was a correlation between the size of the catalyst and the efficiency 10 of the overall system or useful life of the catalyst. Some materials are also preferred for their chemical properties, i.e., their "inertness" or "promoting" properties.

The support serves a number of functions in a 15 heterogeneous catalytic system. Ease of handling is facilitated by a support which generally takes the form of discrete particles or aggregates of varying shape or size which, depending on usage, have a major dimension of about 1 millimeter to about 20 millimeters. Thus it is not necessary for the catalyst to 20 form a permanent or semi-permanent part of the reactor.

The support, however, serves primarily to increase the surface area of the "active" component of 25 the catalyst, silver, which is important in that most epoxidation occurs at the silver surface-fluid interface. Many of the substances commonly employed as catalyst supports not only have the usual external surface, which provides a varying surface area, depending on the shape of the support bodies and the 30 packing of the bodies, but are also of a porous nature and, therefore, have a large internal surface which contributes to the overall surface area of the supported catalyst. Such support materials provide a 35 greater capacity for sorbing not only the catalyst

material during catalyst preparation (when the support is impregnated with a solution containing the catalyst component(s) in soluble form) but also a greater capacity for the flow of the fluid reactants 5 within the catalyst during the reaction for which the catalyst is intended. The support also improves performance by lowering the pressure drop through the reactor and by facilitating heat and mass transfer.

Among the large variety of substances employed 10 in the past as supports for catalytic materials, alumina has exhibited superiority in many respects as a catalyst support material. In addition to the low cost of the material, alumina has good thermal stability and some forms have a relatively large surface 15 area.

Alumina, in its various forms, particularly alpha-alumina, has been preferred as a support material for silver-containing catalysts in the preparation of alkene oxides. Numerous variations of surface area, pore dimensions, pore volume and particle 20 size have been suggested as providing the ideal physical property or combination of properties for improving efficiency, activity or useful life of the catalyst.

Holler (U. S. Patent 3,908,002) discloses an alpha-alumina, useful as a catalyst support for reactions conducted at temperatures below 800 degrees C., such as oxidation reactions of hydrocarbons to oxyhydrocarbons. The support, having a surface area reported to be at least about 40 m<sup>2</sup>/g, is produced by 25 thermally decomposing a porous aluminum ion chain-bridged, polymeric carboxylate. Indicating that a large surface area in a carrier may be detrimental to 30 its efficient operation and catalyst activity, Belon (U. S. Patent 3,172,066) describes a method of pro-

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ducing a macroporous catalyst carrier which may be used in the catalytic production of ethylene oxide having pore diameters of between 0.1 and 8.0 microns and a specific surface area between a few square meters and one square decimeter per gram. The support is prepared by heating a mixture of active and calcined aluminum oxides and a small amount of boron oxide at temperatures of between about 1,600 and 1,800 degrees C. Waterman (U. S. Patent 2,901,441) describes a process for preparing highly active and selective catalysts for the oxidation of olefins to olefin oxides on a support having an average porosity of at least 35 percent. The method involves washing an alpha-alumina or silicon carbide support having an average porosity of between 35 and 65 percent with an aqueous solution of lactic acid, washing with water until neutral, and then impregnating the support with an aqueous solution of silver lactate. The impregnated support is thereafter heat-treated to deposit elemental silver. A silver-supported catalyst for the vapor phase oxidation of ethylene to ethylene oxide, exhibiting improved production of ethylene oxide and catalyst longevity, is described by Brown et al (U. S. Patent 3,725,307). The catalyst is disclosed as being formed from support particles having an average pore diameter of at least 10 microns up to, preferably, 70 microns and a surface area of less than about 1 m<sup>2</sup>/g. The selectivities reported do not range above about 73 percent. The support is preferably composed of silica-alumina. A silver-supported catalyst which includes a support of alpha-alumina, silicon carbide, fused aluminum oxide, or mixtures of alumina and silica was asserted by DeMaio (U. S. Patent 3,664,970) to eliminate the need for halogenated inhibitors in the oxidation of ethy-

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lene to ethylene oxide. The support is composed of particles having a minimum apparent porosity of about 30 percent and wherein at least 90 percent of the pores have diameters in the range of 1 to 30 microns, 5 the average of the diameters being in the range of 4 to 10 microns. Wattimena (U. S. Patent 3,563,914) discloses silver catalysts using aluminum oxide supports having pore volumes between 0.15 and 0.30 cc/g and surface areas below about  $10 \text{ m}^2/\text{g}$ .

10 Hayden et al (U. K. Patent Application 2,014,133) disclose a silver catalyst employing a support having a specific surface area in the range of 0.05 to  $10 \text{ m}^2/\text{g}$ , an apparent porosity of at least 20 percent, and mean pore diameters of 0.1 to 20 15 microns, the pore size distribution being bimodal, in which the smaller pores preferably account for at least 70 percent of the total pore volume. Alpha-alumina supports are described by Rashkin (U. K. Patent Application 2,122,913A) having a "relatively low surface area" of less than  $30 \text{ m}^2/\text{g}$ . Mitsuhata et 20 al (Japanese Published Patent Application 56-089843) and Mitsuhata et al (U. S. Patent 4,368,144) describe supported silver catalysts in which the support is formed from alpha-alumina having a specific surface 25 area of 0.5 to  $5 \text{ m}^2/\text{g}$ . Watanabe et al (Japanese Published Patent Application 56-105750) employ a similar catalyst support having a surface area of 1 to  $5 \text{ m}^2/\text{g}$ . Hayden et al (U. S. Patent 4,007,135) describe silver-containing catalysts in which the 30 porous heat-resisting support has a specific surface area in the range of 0.04 to  $10 \text{ m}^2/\text{g}$ , an apparent porosity of at least 20 percent, and a median pore diameter of 0.3 to 15 microns. Mitsuhata et al (U. S. Patent 4,248,740) describe the use of high 35 alpha-alumina content supports having a specific

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surface area of not more than  $10 \text{ m}^2/\text{g}$ , an apparent porosity of 40 to 60 percent by volume, and a pore volume of 0.1 to 0.5 cc/g. Armstrong et al (U. S. Patent 4,342,667) disclose a supported silver catalyst, useful in the oxidation of ethylene to ethylene oxide, in which the support has a surface area of 0.02 to  $2 \text{ m}^2/\text{g}$ , an average pore diameter of 0.5 to 50 microns and an average pore volume of 0.2 to 0.5 cc/g.

5        There has also been some interest in the purity of supports employed, both as to composition and phase. Examples of high purity alumina include U. S. Patent 2,901,441 which uses alpha-alumina having a purity of about 99.5 percent as a support for catalysts used to oxidize olefins to olefin oxides. An ethylene oxidation catalyst is disclosed in German Patent Publication DE 2,933,950 which attains a long catalyst life without a loss in activity or selectivity by using an alpha-alumina support having less than 0.001 weight percent of alkali-soluble silicon compounds. The catalyst is prepared by boiling commercial quality alpha-alumina with 1 weight percent sodium hydroxide solution and washing to a pH value of 8. If desired, the silicon compound concentration may be reduced below 1 part per million (ppm) by washing further with 1 weight percent HF. U. K. Patent Application 2,122,913A describes supported silver catalysts in which the support is composed of silica, alumina or mixtures thereof, one example of which is an alumina having a purity of 99.3 percent by weight. The silver-supported catalyst described in Japanese Published Patent Application 56-089843 employs an alpha-alumina carrier having a sodium content of less than 0.07 weight percent. Japanese Published Patent Application 56-105750 describes the

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use of an alpha-alumina support in conjunction with a silver catalyst for producing ethylene oxide, which support has a sodium content less than 0.07 weight percent. A silver catalyst including an alpha-alumina carrier having a sodium content of not more than 0.07 percent is described by Mitsuhata et al (U. S. Patent 4,368,144). The support also has a surface area within the range of 0.5 to 5 m<sup>2</sup>/g, an apparent porosity of 25 to 60 percent, a specific pore volume of 0.2 to 0.5 cc/g, and a particle diameter within the range of 3 to 20 mm. An alpha-alumina support having a purity of 98+ weight percent, for use with silver in the catalytic oxidation of ethylene, is described by Warner et al in U. S. Patent 4,455,392. The patent additionally discloses that the carrier is generally a conventional microporous support with surface areas of less than 10 m<sup>2</sup>/g, pore volumes ranging from about 0.15 to 0.8 cc/g, and pore diameters of about 0.1 to 100 microns.

In addition to compositional purity, both phase purity and morphology of the support have been areas in which improvements in efficiency, selectivity or stability of the catalyst have been sought. Examples include U. S. Patent 2,901,441 in which aluminum oxide is substantially completely converted to the alpha form of alumina by heating aluminum oxide to a temperature of about 1,500 to 2,050 degrees C. Weiss (U. S. Patent 2,209,908) and Carter (U. S. Patent 2,294,383) describe the use of "Tabular Corundum" as a catalyst support for metallic oxides, such as those oxides of metals selected from the fifth and sixth group of the periodic system, for example, vanadium, molybdenum, uranium, etcetera, in the oxidation of various organic materials to maleic acid and maleic anhydride and silver for the catalytic oxidation of

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ethylene to ethylene oxide, respectively. Weiss indicates that Tabular Corundum, which is almost entirely aluminum oxide and has the alpha-corundum crystalline form of aluminum oxide, may be formed by

- 5 mixing aluminum oxide with one or more of several compounds, such as sodium oxide and chromic oxide, and heating the mixture to a temperature in the range of about 800 to about 1,800 degrees C. Tabular Corundum is further described as having impurities  
10 present in only small quantities, the material also includes "readily bonded surfaces and consisting essentially of interlocked corundum crystals in tabular form, having the contained impurities disseminated in minute globules throughout the crystal-line alumina". Brengle et al (U. S. Patent  
15 2,709,173) also employ Tabular Corundum as a support in one of their examples.

U. S. Patents 4,039,481 and 4,136,063 to Kimura et al disclose a catalyst carrier and a method for  
20 making same, the catalyst being the type used in catalytic converters in automobile exhaust systems. Specifically, the catalysts have a surface layer containing alpha-phase alumina and an inner portion consisting essentially of alumina of a phase other  
25 than that of the alpha phase. The pores in the alpha-alumina surface layer are larger than those in the inner portion of the catalyst body. A method of preparing the phase gradient support particles is described which provides for treating the surface of  
30 the alumina to a depth of about 400 microns with a transition element, particularly iron, and thereafter firing the carrier particles.

Weber et al (U. S. Patent 4,379,134) describe high purity alpha-alumina bodies, at least 85 percent  
35 of the pore volume of the bodies having pores with a

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diameter of from 10,000 to 200,000 Angstroms. The high purity alpha-alumina bodies are prepared by peptizing boehmite in an acidic aqueous, fluoride anion-containing mixture. An extrudable mixture is  
5 formed thereby which is extruded and shaped into formed bodies which are thereafter dried at 100 to 300 degrees C, calcined at a temperature of from 400 to 700 degrees C to convert the alumina to the gamma phase, and subsequently calcined further at a temper-  
10 ature of from 1,200 to 1,700 degrees C to convert the gamma phase to alpha-alumina phase.

A method of producing granulated porous corundum having a homogeneous porous structure with a total pore volume of 0.3 to 1.0 cm<sup>3</sup>/g and a predominant  
15 pore size of 5,000 to 30,000 Å is described by Bores-  
kov et al (U. S. Patent 3,950,507). The method of preparing the alpha-alumina includes treating active alumina or aluminum hydroxide having a porous struc-  
ture to a first heat treatment in which the tempera-  
20 ture is increased from 20 to 700 degrees C, a second heat treatment in the range of from 700 to 1,000 degrees C, and a third treatment in the range of from 1,000 to 1,400 degrees C. Each of the heat treat-  
ments is for a period of at least one-half hour, the  
25 first heat treatment being conducted in an atmosphere of hydrogen fluoride in which the alumina absorbs the hydrogen fluoride and the second heat treatment de-  
sorbs the hydrogen fluoride. The patent also de-  
scribes a similar procedure employing stationary  
30 thermal conditions in which the granules of alumina or aluminum hydroxide are impregnated with other fluorine-containing substances prior to the first thermal treatment. The recommended starting mater-  
ials used to form alpha-alumina include granulated  
35 pseudo-boehmite, boehmite or bayerite as the granu-

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lated aluminum hydroxide and granulated alpha-, eta-, or theta-alumina as the active alumina.

Although alpha-alumina has been considered by most to be the preferred alumina support material,

- 5 Smith et al (U. S. Patent 2,422,172) have suggested that beta-aluminas are more desirable than the alpha phase as a support material for catalysts, particularly those used in catalytic conversion processes such as dehydrogenation and hydroforming.

10 In seeking the ideal support material, there has been some departure from the commonly employed substances. For example, some use has been made of alkali metal and alkaline earth metal carbonates, both as the sole support material and in combination 15 with other materials as the carrier for processes such as direct oxidation of alkenes to epoxides.

- A number of supported silver-containing catalysts have been employed for epoxidation of alkenes in which the carrier includes, sometimes labelled as 20 a promoter, a carbonate of a metal, generally an alkali metal or alkaline earth metal. Some examples of the use of one or more alkali and/or alkaline earth carbonates may be found in U. S. Patents 2,424,084, 2,424,086, 2,615,900, 2,713,586, 25 3,121,099, 3,258,433, 3,563,913, 3,563,914, 3,535,217, 4,007,135, 4,033,903, 4,039,561, 4,066,575, 4,094,889, 4,123,385, 4,125,480, 4,168,247, 4,186,106, 4,226,782, 4,229,321, 4,324,699, European Patent Publications 0,003,642 and 30 0,011,356, Japanese Patents 41-11847 and 57-107242, U. K. Patents 590,479, 1,571,123 and 2,014,133A, and Murray, "A Study Of The Oxidation Of Ethylene TO Ethylene Oxide On A Silver Catalyst", Australian Journal of Scientific Research, Volume 3A, Pages 433-35 449 (1950). In addition, U. S. Patent 3,332,887 to

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Endler employs zinc and/or cadmium carbonates, Gelbstein, (DS 2,352,608) discloses the use of the latter carbonate and European Patent Publication 0,003,642 mentions the use of molybdenum carbonate. Boreskov et al (U. S. Patent 4,130,570) describe a method of producing ethylene oxide using a catalyst which includes silver, cadmium carbonate and/or cadmium oxide and fused alumina. Oprescu et al (French Published Patent Application 2,005,978) describe a silver-based catalyst for use in the preparation of ethylene oxide which is a coprecipitate of silver and other carbonates.

Several patents have described the use of fluorine-containing substances to treat support materials, in some cases to provide a compositionally pure support, and in other cases as a fluxing agent to improve the phase purity of the support. Thus, U. K. Published Patent Specification 590,479 and U. S. Patent 2,424,086 indicate that a more active catalyst is formed if the support material has undergone a preliminary treatment with a dilute solution of hydrofluoric acid prior to impregnation with silver. U. S. Patent 4,379,134 teaches the preparation of high purity alpha-alumina bodies by peptizing boehmite alumina in an aqueous acidic mixture containing fluoride anions and water. German Patent 2,933,950 teaches the reduction of silicon content by treatment with HF. U. S. Patent 3,950,507 teaches the preparation of granulated porous corundum by a multiple step heat treatment in which initial steps may be carried out in an atmosphere of hydrogen fluoride. Hosoda et al (U. S. Patent 3,144,416) suggest that a small amount of a halogen compound, sulfur compound, nitrogen compound, or phosphorous compound may be added either to the reaction gas or the catalyst to improve

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the selectivity of the catalyst.

The nature of the silver itself has also been examined and modified in attempts to improve the efficiency and stability of the catalyst. Cavitt

5 (U. S. Patent 4,229,321) teaches that a supported silver catalyst of improved selectivity and activity may be prepared by mechanically removing the outer surface or skin of the catalyst after the impregnated catalyst has been heated to evaporate volatile material and reduction of the silver salt to silver metal, thereby activating the catalyst.

Since the early work on the direct catalytic oxidation of ethylene to ethylene oxide, workers in the field have suggested that the addition of certain 15 compounds to the gaseous feedstream or direct incorporation of metals or compounds in the catalyst could enhance or promote the production of ethylene oxide. Such metals or compounds have been known variously as "anti-catalysts", "promoters" and "inhibitors". These substances, which are not themselves 20 considered catalysts, have been proposed by prior workers to contribute to the efficiency of the process by inhibiting the formation of carbon dioxide or promoting the production of ethylene oxide. The 25 scientific literature is replete with examples of the use of alkali metals and alkaline earth metals and their cations to promote the efficiency of silver catalysts used in epoxidation reactions. For example, sodium, potassium and calcium were disclosed as being suitable promoters in U. S. Patent 2,177,361. Numerous examples may be found in literature of preference for one or several metals or cations and exclusion of one or more metals or cations as promoters 30 in silver catalysts.

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Among those anions associated with the cation promoters used in preparing silver-containing catalysts employed in direct epoxidation reactions that have been suggested as being suitable include car-  
5 boxylates, for example, formate, acetate, malonate, oxalate, lactate, tartrate, and/or citrate, and inorganic salts, such as carbonates, bicarbonates, phosphates, nitrates, and/or nitrites, chlorides, iodides, bromates, and isopropoxides. However, al-  
10 though many examples may be found in the literature indicating that such compounds are suitable, numerous patents, such as U. S. Patents 3,962,136; 4,012,425; 4,066,575; 4,207,210; and 4,471,071, suggest that no unusual effectiveness, particularly with regard to  
15 catalytic activity, is observed with any particular anion of an alkali metal promoter. U. S. Patents 4,007,135; 4,094,889; 4,125,480; 4,226,782; 4,235,757; 4,324,699; 4,342,667; 4,356,312; 4,368,144; and 4,455,392 disclose that potassium  
20 nitrate may be added to the catalyst as a suitable promoting material. Potassium nitrate may also be formed in situ when a carrier material is treated with certain amines in the presence of potassium ions as, for instance, when silver is introduced to a  
25 carrier material in a silver-impregnating solution containing an amine and potassium ions, followed by roasting.

A number of compounds have been proposed in the literature as additives to the feedstream or re-  
30 actants to improve the efficiency of the direct, silver-catalyzed oxidation of alkenes to alkene oxides. For example, Law and Chitwood (U. S. Patent 2,194,602) disclose the use of a "repressant", i.e., anti-catalyst, such as ethylene dichloride, chlorine,  
35 sulfur chloride, sulfur trioxide, nitrogen dioxide,

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or other halogen-containing or acid-forming materials. Numerous additional anti-catalysts are presented by the same patentees in U. S. Patent 2,279,469. The anti-catalysts, broadly listed in 5 categories such as halogens and compounds containing halogen, hydrocarbons, compounds containing carbon, hydrogen and oxygen, compounds containing sulfur, and compounds containing nitrogen are represented and, in addition to those compounds already mentioned above, 10 additional representative compounds include, as nitrogen-containing compounds, nitric oxide, ammonia, amines such as ethylenediamine, diphenylamine and analine, nitro compounds such as o-nitroanisole and o-nitrotoluene as organic oxygen-containing organic 15 compounds, alcohols such as methyl, ethyl and iso-propyl alcohols, ethers such as isopropyl and dibutyl ethers, as well as g<sub>1</sub>,<sub>3</sub>ol ethers, ketones such as methyl ethyl ketone and acetone, as hydrocarbons such as benzene, and N-hexane; sulfur compounds such as 20 sulfur dioxide, hydrogen sulfide and diethylsulfide; chlorine-containing compounds such as carbon tetrachloride, chlorobenzene and dichloroethyl ether. Berl (U. S. Patent 2,270,780) lists a number of compounds as anti-detonating or anti-knock materials to 25 control the oxidation of ethylene and propylene to their oxides. Disclosures of other feedstream additives used in the production of alkene oxides, particularly halogen compounds, may be found in U. S. Patents 2,279,470; 2,799,687; 3,144,416; 4,007,135; 30 4,206,128; and 4,368,144. In addition, EPO Patent 0,003,642 and U. K. Patent Application 2,014,133A disclose processes for the production of olefin oxides employing silver-containing catalysts in which a chlorine-containing reaction modifier and a nitrite 35 or nitrite-forming substance are described. Rumanian

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Patent 53012, published December 2, 1971, discloses a direct, silver-catalyzed direct epoxidation procedure which employs oxides of nitrogen in the feedstream. U. K. Patent 524,007 includes ethylene dichloride or 5 nitrogen dioxide in the feedstream of a silver-catalyzed epoxidation procedure.

Although much of the art discussed above has resulted in improvements in the efficiency, activity or stability of the catalytic system, many of the 10 improvements have individually been rather slight. In some of the catalytic systems, gains in one of these performance parameters have been frequently offset by losses in another; that is, enhancement of one index of performance has been accompanied by a 15 deleterious effect on another of the indices. For example, if a reaction system is designed which has a very short useful life, the system may be commercially impractical even though the efficiency and initial activity of the catalyst are outstanding. 20 Accordingly, a system that provides an increase in the efficiency of the overall catalytic reaction system, while only minimally decreasing the activity and useful life of the catalyst, would be particularly beneficial as would a system in which the useful 25 life is improved at little expense to the efficiency or activity.

Disclosure Of The Invention:

30 The present invention is directed to catalytic processes for the epoxidation of alkene in the presence of an oxygen-containing gas and to the catalyst used therefor. The process comprises contacting an alkene with an oxygen-containing gas under epoxidation 35 conditions in the presence of at least one gas-

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eous efficiency-enhancing member of a redox-half reaction pair and a solid catalyst. The catalyst comprises a catalytically effective amount of silver on a solid porous support and an efficiency-enhancing 5 amount of at least one efficiency-enhancing salt of a member of a redox-half reaction pair. The support employed for the catalyst comprises at least one carbonate salt of barium, strontium, calcium, magnesium, or mixtures thereof. The porous support may 10 be either one which consists essentially of a carbonate salt or one in which the carbonate salt is associated with an inert substructure, such as alumina.

The present invention is also directed to a catalyst for use in epoxidation of alkene with an 15 oxygen-containing gas which comprises a catalytically effective amount of silver on a solid support and at least one efficiency-enhancing salt of a member of a redox-half reaction pair. The combination of a porous support comprising a carbonate salt and the presence 20 of a salt of a member of a redox-half reaction pair produces a catalyst of enhanced performance which is both highly active and capable of maintaining such activity for extended periods of time. In addition to these indices of performance, a catalytic 25 system employing such a catalyst, particularly when used in the presence of a gaseous member of a redox-half reaction pair, also results in enhancement of efficiency. Thus, efficiencies on the order of about 30 84 percent for the epoxidation of ethylene are the norm under Standard Test Conditions and of about 88-92 percent or greater are not uncommon. In addition, the catalysts of the present invention are capable of maintaining high activity well as long term stability.

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Detailed Description Of The Invention:

The present invention is directed to a process for the vapor phase oxidation of alkenes to alkene 5 oxides, i.e., an epoxidation process, in the presence of an oxygen-containing gas and to the silver catalysts employed therein.

The process and catalyst of the present invention are useful in the epoxidation of the alkenes 10 ethylene and propylene, the epoxides of which are in great demand for use as intermediates in producing such materials as polymers, surfactants, synthetic fibers and antifreeze. However, the present invention is not limited to these compounds but may be 15 used to oxidize cyclic and acyclic alkenes which are in the gaseous state or have significant vapor pressures under epoxidation conditions. Typically these compounds are characterized as having on the order of 12 carbon atoms or less which are gaseous under epox- 20 idation conditions. In addition to ethylene and propylene, examples of other alkenes which may be used in the present invention include such compounds as butene, dodecene, cyclohexene, 4-vinylcyclohexene, styrene and norbornene.

25

Support:

The support material used in the present invention may be selected from one of several carbonate-containing carrier materials. In each embodiment of 30 carrier, the carbonate employed is an inorganic carbonate, preferably having a cation which is an alkaline earth metal ion, particularly calcium, strontium, magnesium or barium with calcium being most 35 preferred. The carriers of the present invention may

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exist in various forms. In one embodiment, the carrier is one in which the carbonate is the predominant or, preferably, substantially the exclusive component of the support. In other embodiments of the invention, the inorganic support material is used in conjunction with a solid substrate, i.e., a subsupport or substructure composed of a more conventional support material, such as alumina and preferably alpha-alumina. This latter type of support may employ the 5 carbonate material coated on individual, relatively small particles of substructure or subsupport or on a larger unit such as a three-dimensional framework having a honeycomb-type of structure.

When used with a subsupport, the percentage of 10 carbonate material present in the support material is, by weight, frequently about 0.5 to about 15, based on the weight of the total support. Most often the carbonate is present in an amount of about 2 to 15 about 11 percent, by weight.

A granular or crystalline form of the carbonate support material is preferred in the present invention, particularly when used as the exclusive or predominant component of the support. Commercially available carbonate materials suitable for use in the 20 present invention may be obtained as powders which can be converted to the preferred granular form by forming a paste and spreading it thinly on a flat surface, such as a large tray. After spreading the material on the surface to a suitable depth, usually 25 approximately one-quarter inch, the carbonate material may be dried and calcined at a temperature of from about 25 to about 75 degrees C below the melting or decomposition temperature of the material. In one 30 embodiment the paste of the carbonate mixture is 35 dried and calcined by placing it into a furnace at

about 120 degrees C and heating to about 500 degrees C over a fifteen minute period and holding it at that temperature for an additional fifteen minutes. The calcined carbonate is then broken into smaller pieces 5 and screened to particles of the appropriate size, on the order of one-eighth to three-eighths inch, preferably about one-quarter inch in diameter. As described in greater detail below, the carbonate support may then be impregnated, or coated, with a solution containing a silver compound and thereafter 10 reduced to elemental silver.

Alternatively, as described below, the powdered carbonate material may be combined with an appropriate silver-containing solution, such as that used 15 conventionally to impregnate solid supports to form a slurry or paste. This material may then be spread on a suitable surface and dried and roasted at an appropriate temperature, such as about 500 degrees C, on a belt roaster. This results in a carbonate support 20 with silver being supported thereon in its elemental state. The catalyst may then be impregnated with a solution of a salt of a member of a redox-half reaction pair and thereafter dried. As an alternative, the salt of a member of a redox-half reaction 25 pair may be dissolved in the same silver-containing impregnation solution used to form the coating paste or slurry with the carbonate material.

The particulate carbonate particles, whether or 30 not prepared from a silver-containing paste, can be formed into shaped composites suitable for use in alkylene oxide manufacture. The composites may be formed by any suitable technique. For instance, it is possible to form the composites by compressing the particles into a mold having a desired configuration. Suitable pressures may be at least 1,000 psig,

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say about 3,000 to about 20,000 psig. The size of the particles may be selected to be appropriate for the formation of the composite and are often in the range of about 0.001 to about 5 millimeters in major

5 dimension.

When coated catalysts, i.e., those catalysts in which the carbonate material is coated on a substructure, are employed, a slurry of the carbonate material, in either powder or granular form, is mixed with 10 the particles of support material or the honeycomb structure and thereafter dried in an oven. As with the predominant or exclusive carbonate support materials described above, the coated catalysts may also be prepared by using a solution of a silver compound 15 or the silver compound and a salt of a member of a redox-half reaction pair to form the slurry, followed by suitable drying and roasting.

The surface areas of the carbonate support materials generally range from about 0.6 to about 14 20  $\text{m}^2/\text{g}$ , preferably from about 1.5 to about  $10 \text{ m}^2/\text{g}$ . The surface area is measured by the conventional B. E. T. method using nitrogen or krypton described by Brunauer, Emmet and Teller in J. Am. Chem. Soc. 60, 309-16 (1938).

25 The carrier materials of the present invention may generally be described as porous or microporous.

As indicated above, when the carbonate support materials are used in conjunction with a conventional carrier as a substructure, the preferred support 30 material is alpha-alumina. It is also preferred that the alpha-alumina be of high purity, particularly containing a low sodium content, and also be formed from wafer or platelet-type particles, at least some of which form an interpenetrating crystalline matrix, 35 as described in commonly assigned, copending applica-

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tions to Notermann et al, entitled "Improved Catalytic System For Epoxidation Of Alkenes Employing Low Sodium Catalyst Support", having Canadian Application No. 515,864, filed August 13, 1986 and to Naumann et al, entitled "Improved Catalytic System For Epoxidation Of Alkenes", having Canadian Application No. 515,816, filed August 13, 1986.

The carbonate supported particles of the present invention are generally used as individual particles of irregular shape and size. This is true both for the predominant or exclusive carbonate supports as well as the carbonate-coated supports. However, in some instances the supports, particularly the carbonate-coated supports, may have a particular shape and size and this is especially true of the subsupports used with the carbonates. Typically the subsupports are formed into aggregates or "pills" of a size and configuration to be usable in commercially operated ethylene oxide tubular reactors. These pills may be formed by conventional extrusion and firing techniques. The pills generally range in size from about 2 mm to about 15 mm, preferably about 3 mm to about 12 mm. The size is chosen to be consistent with the type of reactor employed. In general, in fixed bed reactor applications, sizes ranging from about 3 mm to about 10 mm have been found to be most suitable in the typical tubular reactors used in commerce. The shapes of the carrier aggregates useful for purposes of the present invention can vary widely. Common shapes include spheres and cylinders, especially hollow cylinders. Other shapes include amphora (such as defined in U.S. Patents 3,848,033, 3,966,639 and 4,170,569), amorphous, Raschig rings, saddles, cross-partitioned hollow cylinders (e.g., having at least

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one partition extending between walls), cylinders having gas channels from side wall to side wall, cylinders having two or more gas channels, and ribbed or, finned structures. While the cylinders are often 5 circular, other cross-sections, such as oval, hexagonal, quadrilateral, trilateral, etcetera, may be useful.

Catalysts:

- 10 As indicated above, the catalysts of the present invention may include, as a support material, at least one carbonate of or an alkaline earth metal cation, preferably Mg, Ca, Ba or Sr, most preferably 15 Ca. The support may be present either as predominantly or exclusively the carbonate, designated herein as "carbonate-support". The corresponding catalyst which includes such support is designated "carbonate-supported catalyst". When the carbonate 20 is coated on or in the presence of a substrate or subsupport, the support is designated "carbonate-coated support" and when the support is used in a complete catalyst, the designation for the catalyst is a "carbonate-coated catalyst". As used herein, 25 the term "coated" is not intended to imply that one substance necessarily forms a layer on or envelops a second substance but merely refers to the procedure involved in the preparation of such material.
- The carbonate- and carbonate-coated supports may 30 be prepared as indicated above or, when a carbonate support is used, obtained commercially. The carbonate-supported catalyst of the present invention may be prepared by any known method of introducing silver and/or a salt, such as a salt of a redox-half 35 reaction pair, in soluble form, to a support. A

preferred method of introducing silver to the carbonate support is by an impregnation process in which a solution of a soluble salt or complex of silver in an amount sufficient to deposit the desired weight of  
5 silver upon the carrier is dissolved in a suitable solvent or "complexing/solubilizing" agent. The solution may be used to impregnate the support or carrier by immersing the carrier in the silver-containing impregnating solution and forming a pasty  
10 mixture or slurry. The slurry is then spread on a flat inert surface, such as a tray, to a suitable depth of about one-sixteenth to about one-quarter inch, preferably a thickness of about one-eighth inch. This carbonate/silver compound mixture is then  
15 dried and roasted by placing the mixture in a furnace at about 100 to about 120 degrees C and heating the mixture to about 400 to about 600 degrees C over a fifteen minute period, thereafter holding the mixture at a temperature within this range for an additional  
20 fifteen minutes and removing the calcined material from the furnace. This procedure accomplishes drying of the carbonate/silver mixture, removes volatile components and reduces the silver present to its elemental form.

25 The salt of a redox-half reaction pair may be introduced to the catalyst as an impregnation solution in a separate impregnation step. Again, this may be done by any known manner of impregnating a porous material. Conveniently, this may be carried  
30 out by placing the catalyst material in a container, evacuating the container and thereafter introducing the solution of a salt of a member of a redox-half reaction pair. Alternatively, the support may be sprayed or sprinkled with the impregnating solu-  
35 tion. The excess solution may then be allowed to

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drain off or the solvent may be removed by evaporation under reduced pressure at a suitable temperature. The catalyst may then be dried at 120 degrees C in an oven for two hours. Such a procedure is  
5 known as a "sequential" or "consecutive" method of preparation. The carbonate-supported catalyst may also be prepared by a "simultaneous" or "coincidental" method of preparation. With this method, the salt of a member of a redox-half reaction pair is  
10 included in the silver compound-containing solution used to impregnate the carbonate support.

The carbonate-coated catalysts are prepared by coating a suitable substructure or subsupport material, preferably alumina, and most preferably alpha-alumina, with a carbonate-containing slurry. This may contain only the carbonate, in which case the carbonate-coated support is further treated as indicated above to produce a silver or a silver/salt of a redox-half reaction pair carbonate-coated catalyst.  
15 Alternatively, a carbonate/silver compound slurry or a carbonate/silver compound/salt of a member of a redox-half reaction pair slurry in a sequential or coincidental procedure. Thus, in a sequential procedure, particles or pills of a suitable subsupport material, such as alpha-alumina, are coated with a slurry of a carbonate material and a soluble salt or complex of silver dissolved in a complexing/solubilizing agent. The particles or pills are thereafter drained and calcined in an oven at a temperature of about 250 to about 600 degrees C for about three minutes to about four hours, the duration of heating being inversely proportional to the temperature employed. The catalyst is then impregnated in the manner described above with a solution of at least one salt of a member of a redox-half reaction  
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pair and then dried. The carbonate-coated supports may also be formed by a coincidental procedure in which a carbonate/silver compound/salt of a member of a redox-half reaction pair slurry is used to coat particles or pills of a suitable subsupport. After draining, the catalyst is dried at a temperature and for a duration indicated above for those carbonate-coated catalysts prepared by the sequential procedure. The particular silver salt or compound used to form the silver-containing impregnating solution in a solvent or a complexing/solubilizing agent is not particularly critical and any silver salt or compound generally known to the art which is both soluble in and does not react with the solvent or complexing/-solubilizing agent to form an unwanted product may be employed. Thus, the silver may be introduced to the solvent or complexing/solubilizing agent as an oxide or a salt, such as nitrate or carboxylate, for example, an acetate, propionate, butyrate, oxalate, malonate, malate, maleate, lactate, citrate, phthalate, generally the silver salts of higher fatty acids, and the like.

The chemical practitioner may choose from a large number of suitable solvents or complexing/solubilizing agents to form the silver-containing impregnating solution. Besides adequately dissolving the silver or converting it to a soluble form, a suitable solvent or complexing/solubilizing agent should be capable of being readily removed in subsequent steps, either by a washing, volatilizing or oxidation procedure, or the like. The complexing/solubilizing agent, preferably, should also permit solution to provide silver in the finished catalyst to the extent of about 2 to about 60 percent silver or higher, based on the total weight of the catalyst. It is

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also generally preferred that the solvents or complexing/solubilizing agents be readily miscible with water since aqueous solutions may be conveniently employed. Among the materials found suitable as solvents or complexing/solubilizing agents for the preparation of the silver-containing solutions are alcohols, including glycols, such as ethylene glycol (U. S. Patents 2,825,701 to Endler et al and 3,563,914 to Wattimena), ammonia (U. S. Patent 2,463,228 to West et al), amines and aqueous mixtures of amines (U. S. Patents 2,459,896 to Schwartz, 3,563,914 to Wattimena, 3,702,259 to Nielsen, and 4,097,414 to Cavitt, and carboxylic acids, such as lactic acid (U. S. Patents 2,477,435 to Aries and 3,501,417 to DeMaio).

Typically, a silver-containing solution is prepared by dissolving silver in a suitable solvent or complexing/solubilizing agent as, for example, a mixture of water, ethylenediamine, oxalic acid, silver oxide, and monoethanolamine. The solution is then mixed with support particles and drained. Thereafter the particles are suitably dried.

As indicated above, after impregnation, the silver-impregnated carrier particles are treated to convert the silver salt or complex to silver metal and thereby effect deposition of silver on the surface of the support. As used herein, the term "surface", as applied to the support, includes not only the external surfaces of the carrier but also the internal surfaces, that is, the surfaces defining the pores or internal portion of the support particles. This may be done by treating the impregnated particles with a reducing agent, such as oxalic acid or alkanolamine and/or by roasting, at an elevated temperature to decompose the silver compound and reduce

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the silver to its free metallic state.

The concentration of silver in the finished catalyst may vary from about 2 percent to 60 percent, by weight, based on the total weight of the catalyst,

- 5 more preferably the silver concentration ranges from about 8 percent to about 50 percent, by weight. When a "high silver" content catalyst is preferred, the silver ranges from about 30 to about 60 percent, by weight. The preferred concentration for "low silver"
- 10 content catalyst ranges from about 2 to about 20 weight percent. Lower silver concentrations are preferred from a capital expense standpoint. However, the optimum silver concentration for a particular catalyst should also take into consideration
- 15 increased productivity resulting from performance characteristics, such as catalyst activity, system efficiency and the rate of catalyst aging. In many instances higher concentrations of silver are preferred since they demonstrate levels of enhanced performance, particularly catalyst stability, which
- 20 compensates for the greater capital expenditure.

Efficiency-Enhancing Compound:

- 25 A preferred aspect of the present invention includes an efficiency-enhancing amount of at least one efficiency-enhancing salt of a member of a redox-half reaction pair. The term "redox-half reaction" is defined herein to mean half-reactions like those
- 30 found in equations presented in tables of standard reduction or oxidation potentials, also known as standard or single electrode potentials, of the type found in, for instance, "Handbook of Chemistry", N. A. Lange, Editor, McGraw-Hill Book Company, Inc.,
- 35 pages 1213-1218 (1961) or "CRC Handbook of Chemistry

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and Physics", 65th Edition, CRC Press, Inc., Boca Raton, Florida, pages D155-162 (1984). The term "redox-half reaction pair" refers to the pairs of atoms, molecules or ions or mixtures thereof which  
5 are depicted as undergoing oxidation or reduction in such half-reaction equations. A member of a redox-half reaction pair is, therefore, one of the atoms, molecules or ions that appears in a particular redox-half reaction equation. Such terms as redox-half  
10 reaction pairs or like terms are used herein to include those members of the class of substance which provide the desired performance enhancement, rather than a mechanism of the chemistry occurring. Preferably, such compounds, when associated with the catalyst as salts of members of a half-reaction pair, are salts in which the anions are oxyanions, preferably an oxyanion of a polyvalent atom; that is, the atom of the anion to which oxygen is bonded is capable of existing, when bonded to a dissimilar atom, in different valence states. Potassium is the preferred cation and the preferred anions are nitrate, nitrite and other anions capable of undergoing displacement or other chemical reaction and forming nitrate anions under epoxidation or catalyst preparation conditions. Preferred salts include  $\text{KNO}_3$  and  $\text{KNO}_2$ , with  $\text{KNO}_3$  being most preferred.  
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Introduction Of Efficiency-Enhancing Salt To The Carrier:

30       The efficiency-enhancing salt of a member of a redox-half reaction pair may be introduced to the catalyst in any known manner. Thus, impregnation and deposition of silver and an efficiency-enhancing salt  
35       of a member of a redox-half reaction pair may be

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effected coincidentally or sequentially, as described above under the heading "Catalysts". When more than one salt of a member of a redox-half reaction pair is employed, they may be deposited together or sequentially. It is preferred, however, to introduce the salts to the support in a single solution, rather than use sequential treatments using more than one solution and a drying step between impregnation steps, since the latter technique may result in leaching of the first introduced salt by the solution containing the second salt. Typical, and in many cases preferred, of such methods include concurrent, or coincidental, impregnation in which the solution which is used to impregnate the support with silver also contains at least one dissolved efficiency-enhancing salt member of a redox-half reaction pair. This procedure permits introduction of both the silver compound and the efficiency-enhancing salt simultaneously to the support in a single step and solution.

The other commonly employed method is the sequential impregnation of the support in which initial introduction of the silver-containing solution or efficiency-enhancing salt solution (depending upon the sequence employed) is followed by drying of the silver-containing support (and heating and/or chemical reduction of the silver if this is the first added substance). This support is then impregnated with a solution of the second substance, that is, the efficiency-enhancing salt (if the silver was the first added substance).

In order to perform the former procedure, i.e., coincidental impregnation, the efficiency-enhancing salt must be soluble in the same solvent or complexing/solubilizing liquid used with the silver-impreg-

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nating solution. With the sequential procedure in which the silver is added first, any solvent capable of dissolving the salt which will neither react with the silver nor leach it from the support is suitable. Aqueous solutions are generally preferred, but organic liquids, such as alcohols, may also be employed. Suitable procedures for effecting introduction of the efficiency-enhancing salt to the solid support may be found in many of the patents listed above.

The salt of a member of a redox-half reaction pair is added in an amount sufficient to enhance the efficiency of the epoxidation reaction. The precise amount will vary depending upon such variables as the gaseous efficiency-enhancing member of a redox-half reaction pair used and concentration thereof employed in the epoxidation procedure, the concentration of other components in the gas phase, the amount of silver contained in the catalyst, the surface area of the support, the process conditions, e.g., space velocity and temperature, and morphology of support. Generally, however, a suitable range of concentration of the added efficiency-enhancing salt, calculated as cation, is about 0.01 to about 5 percent, preferably about 0.02 to about 3 percent, by weight, based on the total weight of the catalyst. Most preferably the salt is added in an amount of about 0.03 to about 2 weight percent.

It has been noted that when conventional analyses have been conducted with catalysts prepared by co-impregnation with silver and efficiency-enhancing salt, not all the anion associated with the cation has been accounted for. For example, catalysts prepared by co-impregnation with a potassium nitrate solution have been analyzed by conventional tech-

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niques and about 3 moles of the nitrate anion have been observed for every 4 moles of the potassium cation. This is believed to be due to limitations in the conventional analytical techniques and does not necessarily mean that the unaccounted for anions are not nitrate. For this reason, the amount of the efficiency-enhancing salt in the catalyst is given, in some instances, in terms of the weight percentage of the cation of the efficiency-enhancing salt (based on the weight of the entire catalyst), with the understanding that the anion associated with the cation is also present in the catalyst in an amount roughly proportional (on a molar basis) to the cation.

15 Epoxidation Procedure:

As in conventional processes of this type, an alkene and an oxygen-containing gas are brought together in a reactor in the presence of a suitable epoxidation catalyst under epoxidation conditions. Typical epoxidation conditions include temperatures within the reaction zone of the reactor on the order of about 180 to 300 degrees C and pressures from about 1 to about 30 atmospheres.

25 The gaseous efficiency-enhancing member of a redox-half reaction pair may generally be supplied to the reaction zone within the reactor by introducing the component to the feedstream containing alkene and oxygen. Under commercial epoxidation conditions, such as those used in the present invention, the feedstream also contains a gas phase halogen compound, such as an alkyl halide, a hydrocarbon, and, when the effluent stream from the reactor is recycled, unreacted alkene. When recycle of the effluent stream is used, carbon dioxide may also be pres-

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ent. The presence and amount of carbon dioxide depends on, among other things, whether a scrubbing device is used in the process and, if so, to the extent it remains carbon dioxide.

- 5       The terms "gaseous member of a redox-half reaction pair", "gaseous efficiency-enhancing member of a redox-half reaction pair", or like terms referred to herein have a meaning similar to that for the "salt of a member of a redox-half reaction pair" or like terms, defined above. That is, these terms refer to members of half-reactions, represented in standard or single electrode potential tables in standard reference texts or handbooks which are in a gaseous state and are substances which, in the 10 reaction equations represented in the texts, are either oxidized or reduced. The preferred gaseous efficiency-enhancing materials are compounds containing an element capable of existing in more than two valence states, preferably nitrogen, and 15 another element which is, preferably, oxygen. Examples of preferred gaseous efficiency-enhancing members of a redox-half reaction pair include at least one of NO, NO<sub>2</sub>, N<sub>2</sub>O<sub>4</sub>, N<sub>2</sub>O<sub>3</sub> or any gaseous substance capable of forming one of the 20 aforementioned gases, particularly NO and NO<sub>2</sub>, under epoxidation conditions, and mixtures of one of the foregoing, particularly NO, with one or more of CO, PH<sub>3</sub>, SO<sub>3</sub> and SO<sub>2</sub>. NO is most preferred as the gaseous efficiency-enhancing member of a redox-half 25 reaction pair.  
30       Although in some cases it is preferred to employ members of the same half-reaction pair in the reaction system, i.e., both the efficiency-enhancing salt member associated with the catalyst and the gaseous member in the feedstream, as, for example, with a 35

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preferred combination of potassium nitrate and nitric oxide, this is not necessary in all cases to achieve satisfactory results. Other preferred combinations, such as  $\text{KNO}_3/\text{N}_2\text{O}_3$ ,  $\text{KNO}_3/\text{NO}_2$ ,  $\text{KNO}_3/\text{N}_2\text{O}_4$ ,  $\text{KNO}_2/\text{NO}$ ,  
5  $\text{KNO}_2/\text{NO}_2$ , and  $\text{KNO}_3/\text{a mixture of SO}_2 \text{ and NO}$ , may also be employed in the same system. In some instances, the salt and gaseous members may be found in different half-reactions which represent the first and last reactions in a series of half-reaction equations of  
10 an overall reaction.

The gaseous efficiency-enhancing member of a redox-half reaction pair is also present in an amount sufficient to enhance the performance, such as the activity of the catalyst, and, particularly, the  
15 efficiency of the epoxidation reaction. The precise amount is determined, in part, by the particular efficiency-enhancing salt of a member of a redox-half reaction pair used and the concentration thereof, the particular alkene undergoing oxidation, and by other  
20 factors noted above which influence the amount of efficiency-enhancing salt of a member of a redox-half reaction pair. Typically, a suitable concentration of the gaseous member of a redox-half reaction pair for epoxidation of most alkenes, including propylene,  
25 is about 0.1 to about 2,000 ppm, by volume, when  $\text{N}_2$  is used as ballast. When a preferred gaseous member of a redox-half reaction pair, such as NO, is used in the epoxidation of propylene, the preferred concentration is about 5 to about 2,000 ppm, by  
30 volume, with an  $\text{N}_2$  ballast. However, when ethylene is being oxidized, a suitable concentration is in the range of from about 0.1 to about 100 ppm, by volume, of the gaseous feedstream components. Preferably, when ethylene is being oxidized, the gaseous  
35 efficiency-enhancing member of

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a redox-half reaction pair is present in an amount of about 1 to about 80 ppm when about 3 percent, by volume, CO<sub>2</sub> is present. When nitric oxide is employed as the gaseous efficiency-enhancing member 5 of a redox-half reaction pair in an ethylene epoxidation system, it is present in an amount of about 0.1 to about 60 ppm, preferably about 1 to about 40 ppm, when CO<sub>2</sub> is present.

The "oxygen-containing gas" employed in the 10 reaction may be defined as including pure molecular oxygen, atomic oxygen, any transient radical species derived from atomic or molecular oxygen capable of existence under epoxidation conditions, mixtures of another gaseous substance with at least one of the 15 foregoing, and substances capable of forming one of the foregoing under epoxidation conditions. Such oxygen-containing gas is typically introduced to the reactor either as air, commercially pure oxygen or other substance which under epoxidation conditions 20 both exists in a gaseous state and forms molecular oxygen.

The gaseous components which are supplied to the reaction zone, or that region of the reactor where reactants and catalyst are brought together under 25 epoxidation conditions, are generally combined before being introduced to the reactor. The reactors in which the process and catalyst of the present invention are employed may be of any type known to the art. A brief description of several of the reactor 30 parameters which may be used in the present invention are presented below.

In addition to an alkene, oxygen, and the gaseous efficiency-enhancing member of a redox-half reaction pair, the feedstream also contains a performance-enhancing halogen-containing compound, pref- 35

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erably an organic halide, including both saturated and unsaturated halides, such as ethylene dichloride, ethyl chloride, vinyl chloride, methyl chloride and methylene chloride. Preferably, in commercial pro-

5 duction, ethylene dichloride is employed as the halogen-containing compound. The amount of halide em-  
ployed will vary depending upon a variety of factors, including the particular alkene being oxidized and  
10 the concentration thereof, the particular efficiency-  
enhancing salt and gaseous members of redox-half  
reaction pairs and the concentrations thereof, as  
well as other factors noted above as influencing the  
amount of efficiency-enhancing salt and gaseous com-  
pound. However, a suitable range of concentration  
15 for the halogen-containing compound in the oxidation  
of most alkenes, including propylene, is typically  
about 0.1 to about 2,000 ppm, by volume, of the gas-  
eous makeup feedstream. When ethylene is oxidized,  
the range of concentration for the halogen-containing  
20 compound is, however, about 0.1 to about 60 ppm, by  
volume. In addition, a hydrocarbon, such as ethane,  
may be included in the feedstream. The feedstream  
may also contain a ballast or diluent, such as nitro-  
gen, or other inert gas, particularly when air is  
25 used as the oxygen-containing gas. Varying amounts  
of carbon dioxide and water vapor may also be pres-  
ent, depending upon whether means have been provided  
to remove such substances from the effluent stream  
prior to combination of at least a portion of the  
30 effluent stream with the inlet stream. Other than  
the gaseous efficiency-enhancing member of a redox-  
half reaction pair, the components are typically  
present in amounts shown in the following tables for  
propylene and ethylene.

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	<u>Component</u>	<u>Volume Percent (or ppm) for Propylene Oxidation</u>
	propylene	about 2 to about 50
5	oxygen	about 2 to about 10
	alkyl halide	about 5 to about 2,000 ppm
10	hydrocarbon	0 to about 5
	carbon dioxide	up to about 15
	nitrogen or other ballast gas, e.g., methane	remainder.
20	<u>Component</u>	<u>Volume Percent (or ppm) for Ethylene Oxidation</u>
	ethylene	at least about 2, often about 5 to about 50
25	oxygen	about 2 to about 8
	alkyl halide	about 0.1 to about 60 ppm
	hydrocarbon	0 to about 5
30	carbon dioxide	up to about 7
	nitrogen or other ballast gas, e.g., methane	remainder.
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When higher alkenes, such as those previously discussed, are epoxidized, conditions and concentrations typically used for the epoxidation of propylene may be employed.

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Standard Alkene Oxide Process Test Conditions:

The successful commercial production of alkene oxides, particularly ethylene oxide, by the silver-catalyzed oxidation of alkene, particularly ethylene, depends upon a variety of factors. Many of these factors influence, either directly or indirectly, the efficiency of the catalytic system, the activity or the aging rate i.e., stability, of the catalyst. The manner in which catalysts and catalytic systems are evaluated in the laboratory strongly influences the values obtained for these parameters. Techniques and experiments designed to assess such catalysts and catalytic systems commonly employ microreactors (i.e., tiny tubular reactors for testing crushed catalyst particles) or back-mixed autoclaves of the Berty type (i.e., larger reactors which test full-sized catalyst pellets and generally employ full gas recycle) as described in Figure 2 of the article by J. M. Berty, "Reactor For Vapor Phase-Catalytic Studies", Chemical Engineering Progress, 70, Number 5, pages 78-84 (1974), and particularly Figure 2. Microreactors are capable of yielding, in most test situations, the highest efficiency numbers, typically approximately the same as or somewhat greater than those obtainable in commercial tubular reactor operations employing the same catalysts in non-crushed condition. Back-mixed autoclaves commonly provide lower efficiency values because, although conditions can be varied, generally the entire catalyst is ex-

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posed to the outlet gas which has the lowest concentration of reactants and the highest concentration of products. Values obtained using one type of reactor are, seldom identical to those obtained in another  
5 reactor system. As a result, claims of superior results or the desirability of one catalyst over another are preferably based on tests conducted under controlled and comparable conditions.

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- Although the conditions set forth supra may be employed both for reactors employed in commercial production as well as those employed in a laboratory, as a basis of comparison, the catalysts and catalytic systems for epoxidation of ethylene employed in the examples set forth below have been tested under comparable conditions known as Standard Alkene Oxide Process Test Conditions, or Standard Test Conditions (referred to hereinafter as STC). The STC employed for testing and characterizing the catalysts and the catalytic systems of the present invention involve the use of a standard back-mixed bottom-agitated "Magnedrive" autoclave, or Berty autoclave, as described above.
- In discussing the enhancement of efficiency provided by the present invention, it may be noted that, when an efficiency-enhancing amount of a salt of a member redox-half reaction pair is employed, an efficiency for the epoxidation of ethylene of at least about 84 percent is obtained under Standard Test Conditions. "Standard Test Conditions" for ethylene may be defined as comprising the following: by volume, 30 percent C<sub>2</sub>H<sub>4</sub>, 8 percent O<sub>2</sub>, 5 ppm ethyl chloride, 5 ppm, by weight, NO, no added C<sub>2</sub>H<sub>6</sub> or CO<sub>2</sub>, N<sub>2</sub>, ballast, 240 degrees C, 275 psig, gas hourly space velocity (GHSV) = 8,000 hr<sup>-1</sup>.
- Although the present invention can be used with any size and type of alkene oxide reactor, including both fixed bed and fluidized bed reactors known to the art, it is contemplated that the present invention will find most widespread application in standard fixed bed, multi-tubular reactors. These generally include wall-cooled as well as adiabatic or non-wall-cooled reactors. Tube lengths may typically range from about 5 to about 60 feet but will fre-

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quently be in the range of from about 15 to about 40 feet. The tubes may have internal diameters from about 0.5 to about 2 inches and are expected to be typically from about 0.8 to about 1.5 inches. GHSV generally range from about 16,000 to about 1,000 5  $\text{hr}^{-1}$ . Typically GHSV values range from about 2,000 to about 8,000  $\text{hours}^{-1}$  at pressures from about 1 to about 30 atmospheres, commonly about 10 to about 25 atmospheres.

10 While the invention is susceptible to various modifications and alternative forms, certain specific embodiments thereof are described in the examples set forth below. It should be understood, however, that these examples are not intended to limit the invention to the particular forms disclosed but, on the contrary, the invention is to cover all modifications, equivalents and alternatives falling within 15 the spirit and scope of the invention.

20 Example 1 - Preparation Of A  $\text{CaCO}_3$ -Supported  
Catalyst By A Sequential Procedure:

Calcium carbonate in granular form was prepared by combining 300.0 g of powdered calcium carbonate 25 (Baker Analyzed Reagent) and 250.0 g distilled water to form a thick paste which was spread to a thickness of approximate one-quarter inch on a stainless steel tray and calcined at a temperature of about 800 degrees C for sixteen hours. The calcined product was 30 then fractured into fragments which were screened to obtain pieces approximately one-quarter inch in diameter. The particles were impregnated with an aqueous silver amine solution by allowing them to stand in a solution containing 41.2 g ethylenediamine, 40.8 35 g distilled water, 41.2 g oxalic acid, 72.2 g silver

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oxide, and 14.4 g monoethanolamine. The slurry or paste formed from the silver-containing solution and calcium carbonate were spread on a stainless steel tray to a thickness of approximately 1/8 inch. The  
5 mixture was calcined by placing it into a furnace at 120 degrees C and heating to a temperature of 500 degrees C over a fifteen minute period. The mixture was thereafter held at a temperature of 500 degrees C for a fifteen minute period and then removed from the  
10 furnace. Upon cooling, the calcium carbonate supported silver catalyst was impregnated with  $\text{KNO}_3$  by immersing 50.7 g of the catalyst in a solution formed by dissolving 2.03 g  $\text{KNO}_3$  in 100 ml of distilled water. The catalyst particles were dried at 120  
15 degrees C in an oven for two hours. The catalyst contained 40 percent Ag and 0.6 percent K, as determined by analysis.

After autoclave testing for twelve days, the above catalyst was impregnated a second time to increase the  $\text{KNO}_3$  concentration. The catalyst pieces  
20 (47.7 g) were immersed in a solution prepared from 7.6 g  $\text{KNO}_3$  dissolved in 100 ml water. The resulting material was dried at 120 degrees C for a period of two hours. The resulting catalyst had a Ag concentration of 39 percent and a K concentration of 1.7  
25 percent, by weight, based on the total weight of catalyst as determined by analysis.

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Example 2 - Preparation Of A Calcium  
Carbonate-Coated, Potassium Nitrate-Impregnated  
Silver Catalyst By A Coincidental Procedure:

- 5     About 23.5 g of low density (30 pores/inch), irregularly-shaped catalyst support particles of alpha-alumina formed from a honeycomb structure available from High Tech Ceramics, Alfred, New York, having average diameters of 5/8 inch, were coated by
- 10    thoroughly mixing the particles with a slurry formed from calcium carbonate in an aqueous silver amine/potassium nitrate solution for a period of five minutes and then draining. The silver amine solution was prepared by mixing 41.1 g ethylenediamine, 40.8 g
- 15    distilled water, 41.2 g oxalic acid, 71.2 g silver oxide, 14.4 g monoethanolamine, and 6.2 g potassium nitrate. After adding an additional 15 ml distilled water, 51.4 g of Mallinckrodt "prescription grade" calcium carbonate was added with thorough mixing.
- 20    The irregularly-shaped catalyst support particles were then added to the silver amine/calcium carbonate slurry and thoroughly mixed. The excess slurry or liquid was drained and the coated particles were calcined in an oven at 300 degrees C for a period of
- 25    three hours. The catalyst contained 29 percent Ag, 0.7 percent K and 11 percent  $\text{CaCO}_3$ , by weight, based on the total weight of the catalyst.

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Examples 3-5 - Production Of Ethylene  
Oxide With Potassium Nitrate-Containing,  
Calcium Carbonate-Supported Catalysts:

5       The epoxidation reactions described in the examples set forth below were conducted employing catalysts of the type prepared in Example 1. The epoxidation studies for which data are presented below were conducted in a continuously stirred tank reactor, also known as a back-mixed autoclave, of the type described above. The procedure involved charging approximately 80 ml of catalyst to the autoclave. The volume of catalyst was measured in a one inch I.D. graduated cylinder after tapping the cylinder several times to thoroughly pack the catalyst.

10      The back-mixed autoclave was heated to about reaction temperature under a nitrogen atmosphere with the fan of the autoclave operating at about 1,500 rpm. The nitrogen flow was then discontinued and the feed-stream was introduced to the reactor.

15      The back-mixed autoclave was heated to about reaction temperature under a nitrogen atmosphere with the fan of the autoclave operating at about 1,500 rpm. The nitrogen flow was then discontinued and the feed-stream was introduced to the reactor.

20      All ethylene epoxidation reactions, except where indicated otherwise, were examined under Standard Test Conditions comprising, by volume, 30 percent C<sub>2</sub>H<sub>4</sub>, 8 percent O<sub>2</sub>, 5 ppm ethyl chloride, 5 ppm nitric oxide, no added C<sub>2</sub>H<sub>6</sub> or CO<sub>2</sub>, N<sub>2</sub> ballast, 240 degrees C, 275 psig, at a flow rate of 22.6 SCFH, and GHSV = 8,000 hour<sup>-1</sup>.

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TABLE I

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Oxidation Of Ethylene In An  
Autoclave Employing  $\text{CaCO}_3$ -Supported Catalysts

	Example	Percentage Ag	Analyzed Percentage K (K/Ag)	Percentage Ca ( $\text{Ag}/\text{CaCO}_3$ )	Maximum EO Percent	Percent Efficiency	Days Observed
	10						
		3	39	1.7 (0.044)	25 (0.62)	1.0 (4.6 $\times$ $10^{-3}$ )	88
	15	4	22	0.6 (0.027)	30 (0.29)	1.2 (5.2 $\times$ $10^{-2}$ )	89
		5	10	0.5 (0.030)	15 (0.31)	0.9 (7 $\times$ $10^{-1}$ )	89
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Examples 6-19 - Production Of Ethylene Oxide  
With Potassium Nitrate-Containing Calcium  
Carbonate/Alumina-Coated Silver Catalysts:

5       The epoxidation examples set forth below were  
conducted using catalysts prepared in the manner  
described in Example 2, other alkaline earth carbon-  
ates being substituted for CaCO<sub>3</sub> in Examples 14 to  
19. A back-mixed autoclave of the type discussed  
10      above was used for the epoxidation studies for which  
data are presented below. The procedure involved  
charging approximately 80 ml of catalyst to the auto-  
clave. The volume of catalyst was measured in a one  
inch I.D. graduated cylinder after tapping the cylin-  
15      der several times to thoroughly pack the catalyst.  
The back-mixed autoclave was heated to about reaction  
temperature in a nitrogen flow of 11.3 SCFH with the  
fan operating at about 1,500 rpm. The nitrogen flow  
was then discontinued and the feedstream was intro-  
20      duced to the reactor.

An "aging rate", defined as the slope of a plot  
of activity or outlet ethylene oxide (EO) (i.e.,  
 $-d(\%EO)/dt$ , at constant temperature) vs. time, has  
also been provided in Table 2.

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TABLE I

Ethylene Epoxidation In An Autoclave With Potassium Nitrate-  
Containing Alkaline Earth Carbonate  
On Alpha-Alumina Catalyst

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Example	Alkaline Earth Carbonate	Percentage Ag	Percentage K (K/Ag)	Percentage Alkaline Earth (Ag/ Alkaline Earth Carbonate)	Maximum Percent EO (Aging Rate, % EO/day)	Percent Efficiency	
	6	CaCO <sub>3</sub>	29	0.7 (0.026)	11 (1.03)	1.1 (1.3 x 10 <sup>-2</sup> )	88
	7	"	20	1.2 (0.060)	1.7 (6.67)	1.0	89
	8	"	13	0.3 (0.023)	8 (0.65)	1.0 (1.3 x 10 <sup>-2</sup> )	90
	9	"	6	0.05 (0.008)	0.8 (0.80)	0.5 (1.4 x 10 <sup>-1</sup> )	86
	10	"	26	1.02 (0.076)	2.2 (6.16)	1.5 (6.5 x 10 <sup>-4</sup> )	91
	11	"	26	0.46 (0.019)	2.2 (6.16)	1.5	90

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Example 5	Alkaline Earth Carbonate	Percentage Ag	Percentage K (K/Ag)	Percentage Alkaline Earth (Ag/ Alkaline Earth Carbonate)	Maximum Percent EO (Aging Rate, to EO/day)	Percent Efficiency
10	12 "	18	1.4 (0.076)	3.5 (2.12)	1.3 (9.6 x $10^{-4}$ )	90
	13 "	19.0	1.4 (0.076)	0.9 (0.36)	1.3 (9.3 x $10^{-4}$ )	91
	14 <chem>BaCO3</chem>	13	1 (0.076)	2.7 (2.07)	0.75 (1.1 x $10^{-3}$ )	89
15	15 "	16	1.3 (0.08)	3.6 (2.88)	1.7 (7.6 x $10^{-4}$ )	91
	16 "	20	0.6 (0.02)	4.0 (2.87)	1.8 (5.5 x $10^{-4}$ )	91
20	17 <chem>BaCO3</chem>	17	1.6 (0.02)	5.6 (3.13)	1.2 (6.4 x $10^{-4}$ )	90
	18 "	20	0.4 (0.02)	6.4 (2.14)	1.5 (9.0 x $10^{-4}$ )	90
25	19 <chem>MgCO3</chem>	17	0.4 (0.02)	1.0 (0.0)	1.00 (4.5 x $10^{-4}$ )	87

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Examples 20-21 - Preparation Of Pressed  
Alkaline Earth Carbonate-Supported Catalysts  
By A Sequential Procedure:

5 Example 20:

A calcium carbonate catalyst was prepared by combining 30.0 g  $\text{CaCO}_3$  with 81.8 g of a silver-impregnating solution prepared by combining 101.7 g 10 ethylenediamine, 100 g distilled water, 103.8 g oxalic acid, 181.6 g silver oxide, and 38.3 g monoethanolamine and diluting the solution to 500 ml with distilled water. The slurry formed by combination of the calcium carbonate and silver-impregnating solution 15 was placed in a porcelain dish and roasted in a muffle furnace at 300 degrees C for a period of about 16 hours. The dried catalyst was subsequently cooled, removed from the porcelain dish and ground to a powder with a mortar and pestle. The powdered material 20 was placed in a steel die having a diameter of 1 inch and force of 10,000 pounds was applied with a hydraulic press to form the material into a 1 inch diameter wafer having a thickness of about 1/16 to 1/8 inch. Several wafers formed in this manner were 25 then crushed and classified to pass a 14/30 mesh screen.

The catalyst was impregnated with  $\text{KNO}_3$  by immersing 5 g of the catalyst in a solution formed by dissolving 0.20 g  $\text{KNO}_3$  in 90 drops of distilled 30 water. The impregnated material was then dried in an oven at 110 degrees C for a period of about 1 to about 2 hours. The resulting catalyst had a Ag concentration of 40 percent and a  $\text{KNO}_3$  concentration of 4 percent, by weight, based on the total weight of 35 the catalyst.

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Example 21:

A  $\text{KNO}_3$ -impregnated  $\text{SrCO}_3$ -supported catalyst was prepared in the same manner as in Example 20. The same amounts of  $\text{SrCO}_3$  and Ag solution were used to prepare the silver-containing catalyst, 5 g of which was impregnated with a solution containing 0.05 g  $\text{KNO}_3$  dissolved in 55 drops of water. The resulting catalyst had a Ag concentration of 40 percent and a  $\text{KNO}_3$  concentration of 1 percent, by weight, based on the total weight of the catalyst.

Examples 22-23 - Production Of Propylene Oxide With Potassium Nitrate-Containing, Alkaline Earth Carbonate-Supported Catalysts:

The examples of epoxidation set forth below were conducted using catalysts prepared in the manner described in Example 20 and 21. A tubular reactor or microreactor of the type discussed above was used for the epoxidation studies for which data are presented below. For each of the tests, a measured amount of catalyst was placed in the tube of a stainless steel tubular microreactor, the tube having a length of 10.2 centimeters, an outside diameter of 9.52 millimeters, and an inside diameter of 7.75 millimeters. Prior to initiating reaction, the reactor was heated to the preferred temperature, with the catalyst in place, in a flowing nitrogen atmosphere.

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Example 22:

A mixture of gas containing, by volume, 9.67 percent propylene, 9.15 percent oxygen, 200 ppm ethyl chloride, 200 ppm nitric oxide, 1.43 percent methane, and nitrogen as a ballast gas was introduced into a heated tubular reactor at 245 degrees C. The tube of the tubular reactor contained 1 gram (0.9 ml) of 14/30 mesh catalyst at a flow rate of  $1,330 \text{ hr}^{-1}$  at 10 slightly greater than atmospheric pressure. The catalyst had a composition, by weight, of 4 percent  $\text{KNO}_3$  and 40 percent Ag on pressed calcium carbonate. After 155 hours, the outlet propylene oxide concentration (activity) was 1.6 percent with a selectivity of 47 percent.

Example 23:

A mixture of gas containing, by volume, 9.21 percent propylene, 9.06 percent oxygen, 200 ppm ethyl chloride, 200 ppm nitric oxide, 2.21 percent methane, and nitrogen gas as a ballast was introduced to a heated tubular reactor maintained at a temperature of 245 degrees C. The tube of the tubular reactor contained 1 gram (0.8 ml) of 14/30 mesh catalyst at a flow rate of  $1,500 \text{ hr}^{-1}$  at slightly greater than atmospheric pressure. The catalyst employed in the microreactor had a composition of, by weight, 1 percent  $\text{KNO}_3$  and 40 percent Ag on pressed strontium carbonate. After 35 hours, the outlet propylene oxide concentration (activity) was 0.62 percent and the selectivity was 53 percent.

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The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. An improved process for the epoxidation of alkene selected from the group consisting of cyclic and acyclic alkenes containing up to about 12 carbon atoms to form the corresponding alkene oxide wherein said alkene is contacted with oxygen-containing gas in the presence of (i) a performance-enhancing gaseous organic halide compound, (ii) at least one gaseous efficiency-enhancing member of a redox-half reaction pair selected from compounds containing oxygen in combined form with a polyvalent element, (iii) a supported silver catalyst, comprising a catalytically effective amount of silver and an efficiency-enhancing amount of at least one efficiency-enhancing salt selected from the group consisting of salts of oxyanions of polyvalent elements on a support, said oxyanion of said efficiency-enhancing salt and said gaseous efficiency-enhancing member (ii) containing a common polyvalent element and either belonging to the same redox-reaction pair or belonging to different half reaction pairs in a series of chemically-related half reaction equations, and (iv) carbon dioxide, wherein the improvement comprises the support for said catalyst consisting essentially of a carbonate salt selected from the group consisting of the carbonates of barium, strontium, calcium, magnesium, and mixtures thereof.

2. The process of claim 1 wherein said support comprises particles of said carbonate associated with an inert substructure.

3. The process of claim 2 wherein said substructure comprises alumina.

4. The process of claim 3 wherein said substructure comprises alpha-alumina.

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5. The process of claim 2 wherein the support has a surface area of about 0.6 to about 14 m<sup>2</sup>/g.

5. 6. The process of claim 1 wherein the support 5 consists essentially of a carbonate.

7. The process of claim 1 wherein said gaseous and said salt members of a redox-half reaction pair comprise members of the same redox-half reaction and 10 said reaction is conducted in the presence of a performance-enhancing, halogen-containing compound.

8. The process of claim 1 wherein said at least one gaseous member of a redox-half reaction comprises 15 NO, NO<sub>2</sub>, N<sub>2</sub>O<sub>3</sub>, N<sub>2</sub>O<sub>4</sub>, a gas capable of generating one of the aforementioned gases under epoxidation conditions, or mixtures thereof.

9. The process of claim 8 wherein said gas 20 capable of generating one of the aforementioned gases generates at least one of NO and NO<sub>2</sub>.

10. The process of claim 8 wherein said at least one efficiency-enhancing salt of a member of a 25 redox-half reaction pair comprises potassium nitrate.

11. The process of claim 10 wherein the alkene comprises ethylene.

30 12. The process of claim 10 wherein the alkene comprises propylene.

13. The process of claim 1 wherein said at least one gaseous member comprises NO and said at 35 least one salt comprises potassium nitrate.

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14. The process of claim 2 wherein said carbonate is calcium carbonate.

15. A catalyst suitable for epoxidation of alkene in the presence of an oxygen-containing gas comprising a catalytically effective amount of silver on a solid porous support and an efficiency-enhancing salt of a member of a redox-half reaction pair, said solid support comprising at least one carbonate salt selected from the group of carbonates of cations consisting of barium, strontium, calcium, magnesium, and mixtures thereof.

16. The catalyst of claim 15 wherein said support comprises particles of said carbonate associated with an inert substructure.

17. The catalyst of claim 16 wherein said substructure comprises alumina.

18. The catalyst of claim 17 wherein said substructure comprises alpha-alumina.

19. The catalyst of claim 16 wherein the support has a surface area of about 0.6 to about 14  $\text{m}^2/\text{g}$ .

20. The catalyst of claim 15 wherein the support consists essentially of a carbonate.

21. The catalyst of claim 20 wherein said carbonate comprises calcium carbonate.

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22. The catalyst of claim 15 wherein said at least one efficiency-enhancing salt of a member of a redox-half reaction pair comprises potassium nitrate.

5 23. The catalyst of claim 15 wherein said carbonate comprises calcium carbonate.

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